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Patrice LUCAS[1], *Etienne FLEURY*[2], *Jean-François ESTUR*[3], *Vincent LAPINTE*[1], *Jean-Jacques ROBIN*[1*]

[1]Institut Charles Gerhardt, Montpellier, UMR 5253 CNRS- UM2-ENSCM-UM1. Equipe: Ingénierie et Architectures Macromoléculaires, Université Montpellier 2 – Bât. 17 – CC1702, Place Eugène Bataillon, 34095 Montpellier Cedex 5, France.

[2]Laboratoire des Matériaux Macromoléculaires, Ingénierie des Matériaux Polymères,IMP / LMM, UMR CNRS 5223, 17 av. Jean Cappelle, 69621 Villeurbanne, France

[3]Rhodia CRL, 85 Av Frères Perret, F-69190 St Fons Cedex, France

AUTHOR EMAIL ADDRESS: Jean-Jacques.Robin@univ-montp2.fr

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TITLE RUNNING HEAD: Peroxide grafted polysiloxanes

CORRESPONDING AUTHOR FOOTNOTE: Institut Charles Gerhardt Montpellier UMR5253 CNRS-UM2-ENSCM-UM1 - Equipe Ingénierie et Architectures Macromoléculaires, Université Montpellier II, Place Eugène Bataillon, bâtiment 17, case courrier 17-02. 34296 Montpellier Cedex 5, France.

Tel. 33-4-67-14-41-57 Fax. 33-4-67-14-72-20 Jean-Jacques.Robin@univ-montp2.fr

ABSTRACT: Peroxide containing PDMS were synthesized according to a new pathway. Although hydrosilylation is one of the main reaction carried out in silicone chemistry, the catalysts used are very sensitive to the chemical nature of the reactants and remained inefficient to graft allylic peroxide. Radical catalyzed thiol-ene chemistry was involved for the first time to yield an initiator group containing polymer. Peroxide grafted polysiloxane structure and decomposition were characterized using ^{1}H, ^{13}C and ^{29}Si NMR, FT-IR and RAMAN spectroscopies, SEC and DSC. These macroinitiators can be used to obtain polysiloxane able to undergo cross-linking.

KEYWORDS: Polysiloxane, hydrosilylation, peroxide, thiol-ene reaction.

BRIEFS: Peroxide grafted polysiloxanes were synthesized using a non-conventional reaction in the polysiloxane area.

INTRODUCTION

Synthesis of polysiloxane macroinitiator is an interesting starting material for silicone containing copolymers. Various initiator groups were previously linked to polysiloxane either by insertion in the silicon polymer backbone or by grafting onto the polysiloxane backbone. For example, "azo group" were inserted by condensation of azobiscyanopentanoyl chloride with amino terminated polysiloxane[1], and peroxycarbamate groups were introduced by reaction between dihydroxy terminated polysiloxane and an aliphatic hydroperoxide[2]. Bis(silyl pinacolate) groups were inserted in a polydimethylsiloxane backbone by hydrosilylation of a vinyl functional silane containing pinacolic entity with an hydrogen terminated polydimethylsiloxane[3, 4]. Some authors introduced thiuram disulfide group by addition of CS_2 to a α-(secondary amine)-terminated PDMS followed by the addition of a coupling agent (I_2)[5].

The aim of the present research was the synthesis of peroxides containing silicone polymer *via* both the well-known hydrosilylation reaction[6] and the thiol-ene chemistry[7]. The first step was the synthesis of a workable molecule bearing a peroxide function and an unsaturation. The most simple is the *tert*-butyl allyl peroxide (***t*BAP**) synthesized by a phase-transfer catalysis (PTC) process[8]. The effects of numerous factors on the yield of the hydrosilylation of ***t*BAP** reaction were described. The thiol-ene reaction study was divided in two parts: first, the reaction of ***t*BAP** with mercaptopropylsilane monomer (**DM3PSi**) affords functionalized monomer (**BP3DM2Si**). Polycondensation of this monomer with hydroxy-*terminated*-PDMS (**DMS-S15**) yielded peroxide functionalized PDMS. In the second part, direct grafting of ***t*BAP** onto poly[mercaptopropylmethylsiloxane-*co*-dimethylsiloxane] (**SMS-042**) by thiol-ene reaction was described.

EXPERIMENTAL PART

1 – Materials

Tert-butyl hydrogen peroxide, allyl bromide, benzyltriethylammonium chloride (**TEBAC**), methyldimethoxyhydrogenosilane (**MDMHSi**), dichloromethylsilane (**DCMSi**), Speier's catalyst, Karstedt's catalyst, Adam's catalyst, *tert*-butanol, tin(II) ethylhexanoate and Amberlyst 15® were supplied from Aldrich. Bis(dimethylamino)methylsilane (**BDMAmMSi**), poly[dimethylsiloxane-*co*-hydrogenomethylsiloxane] $\mathbf{MD_{85}D'_{0.25}M}$ [M: $(CH_3)_3SiO$, D: $(CH_3)_2SiO$, D': $(CH_3)HSiO$)], dimethoxymethylmercaptopropylsilane (**DM3PSi**), trimethoxymercaptopropylsilane (**TM2PSi**), poly[dimethylsiloxane-*co*-mercaptopropylmethylsiloxane] (**SMS-042**, Mn = 8 300 $g.mol^{-1}$, ≈ 4,7 thiol functions per chain), α,ω-hydroxy-*terminated*-polydimethylsiloxane (**DMS-S15**, Mn = 3 000 $g.mol^{-1}$), α,ω-hydride-*terminated*-polydimethylsiloxane (**DMS-H03**, Mn = 500 $g.mol^{-1}$), 1,1,3,3-tetramethyldisiloxane ($\mathbf{L_2H}$) and hydride-*terminated*-polydimethylsiloxane ($\mathbf{L_nH}$, n = 5, 6) were supplied from ABCR. Bis(4-*tert*-butylcyclohexyl)peroxydicarbonate and AIBN (recristallized from methanol) were supplied from Fluka. Tris(pentafluorophenyl) borane and *cis*-dichlorobis(diethylsulfide) platinum (II) were supplied from Alfa Aesar. Allyl alcohol was supplied by Fluka. Poly[dimethylsiloxane-*co*-hydrogenomethylsiloxane] $\mathbf{MD_9D'_3M}$ (1 008 $g.mol^{-1}$), polyhydrogenomethylsiloxane $\mathbf{MD'_{105}M}$ (8 000 $g.mol^{-1}$) and platinum on carbon were kindly provided by Blue Star. All products were used as received. Solvents were from HPLC grade and stored on sodium.

2 – Analysis

^1H, ^{29}Si and ^{13}C NMR analysis were performed on a Bruker Avance 250 spectrometer using $CDCl_3$ solutions. Chemical shifts are expressed in ppm from internal TMS for ^1H, ^{29}Si and ^{13}C. $Cr(acac)_2$ was added for ^{29}Si NMR analysis. FT-IR analyses were performed on ThermoNicolet Nexus. Differential

Scanning Calorimetry (DSC) analyses were performed under nitrogen with a Perkin Elmer Pyris 1 DSC apparatus calibrated with indium. Thermograms were recorded at 10°C.min^{-1} heating/cooling rate. Activation energy (Ea) and pre-exponential factor (A) were calculated using Differential Scanning Calorimetry in dynamic mode. Isoconversional method based on non-linear regression- was used. Assuming decomposition of the initiator is a single reactive process, nth order reaction f(α) (Fn) was used.

$$\text{Fn: } f(\alpha)=(1-\alpha)^n \quad (1)$$

and $d\alpha/dt=k_d f(\alpha)$ with k_d = dissociation constant (2)

and $k_d=A.e(-E_a/RT)$ with R, the gas constant (8.314 J.mol^{-1}.K^{-1}), T, the Temperature (K) (3)

Combining (1), (2) and (3), it comes:

$$D\alpha/dt= A.e(-E_a/RT).(1-\alpha)^n \quad (4)$$

By computing the data obtained by DSC analyses of the peroxide decomposition and following the previous procedure, the linear regression gave the following result: $k_d=9.89.10^9e(-85/RT)$. Hence, E_a was found to be 85 kJ.mol^{-1}.

Raman spectra were obtained by excitation with 632.8 nm radiation from a He-Ne laser operated at about 17 mW (≈ 12 mW on the sample). The spectra were recorded at 25°C with a LABRAM 1B confocal Raman spectrometer (Jobin-Yvon S.A., Horiba, France). The detector had a two-dimensional array of MPPCCD (1024 x 256 pixels) TE cooled at about -65°C. An optical system mounted on the turret of the microscope was used to work with the laser beam perpendicular to the microscope optical axis. This device allows the macroscopic objectives to work horizontally. The laser beam was focused on the sample by a 50 mm focal lens, and in this case the volume of the illuminated solution was constituted by a cylinder (diameter 250 mm, height 10 mm). The solutions were contained in optical parallepipedic cells filled with 0.2 mL of liquid. Size exclusion chromatography (SEC) analysis were performed on crude samples with a Spectra Physics Instruments SP8810 pump equipped with two 300 mm PL-Gel 5 mm mixed-C columns (Polymer Laboratories) and a Shodex Rise-61 refractometer

detector. Toluene was used as eluent (0.8 mL.min^{-1}) at 30°C. Molecular weights refer to a polystyrene calibration (polystyrene standards from Polymer Laboratories).

3 – Allyl peroxide synthesis: ***t*BAP**

To potassium hydroxide (0.1 mol, 1 eq.) was added **TEBAC** (0.01 mol, 0.1 eq.) and dichloromethane (100 ml). The mixture was kept cold (10°C) with ice during the dropwise addition of *tert*-butyl hydrogen peroxide (0.1 mol, 1 eq.), allyl bromide (0.1 mol, 1 eq.) and dichloromethane (70 ml). Once the addition was over, the mixture was stirred at room temperature for 24 h. A conversion of about 75% was measured by ^{1}H NMR. Dichloromethane was removed by distillation. Pentane was added and the mixture was washed by a 10-wt% potassium hydroxide aqueous solution. Pentane and unreacted allyl bromide were removed by distillation. ***t*BAP** was distilled under reduced pressure (b.p.(20mmHg)=26°C), yield = 70%. Absence of any -OH band of the FT-IR spectra at 3500 cm^{-1} was checked.

***t*BAP**: - (^{1}H NMR 250MHz, $CDCl_3$) δ (ppm): 1.25 (s, $(C\underline{H}_3)_3$-C, 9H), 4.45 (d, $C\underline{H}_2$-CH=CH_2, 2H), 5.20 (m, CH_2-CH=C$\underline{H}_2$, 2H), 5.90 (m, CH_2-C$\underline{H}$=CH_2, 1H) - (^{13}C NMR 250MHz, $CDCl_3$) δ (ppm): 26.6 ($(\underline{C}H_3)_3$-C), 76.2 ($\underline{C}H_2$-CH=), 80.2 ($(CH_3)_3$-$\underline{C}$), 118.7 ($\underline{C}H_2$=CH), 133.3 (-$\underline{C}$H=CH_2).

4 – *Tert*-butyl allyl ether synthesis: ***t*BAE**

Prior to the synthesis, Amberlyst 15® (ion exchange capacity: 4.9 mequiv.) was dried at 90°C for a night. 74 g of *tert*-butanol (1 mol) and 30 g of allyl alcohol (0.5 mol) were mixed together for 24 h at 80°C. The mixture was filtered and the product was purified by elution chromatography (solvent: pentane). ***T*BAE** was distilled (b.p.(760mmHg)=96°C), yield = 20%.

***t*BAE**: - (^{1}H NMR 250MHz, $CDCl_3$) δ (ppm): 1.25 (s, $(C\underline{H}_3)_3$-C, 9H), 3.95 (d, $C\underline{H}_2$-CH=CH_2, 2H), 5.20 (m, CH_2-CH=$C\underline{H}_2$, 2H), 5.90 (m, CH_2-$C\underline{H}$=CH_2, 1H).

5 - Hydrosilylation

All hydrosilylations were performed under argon atmosphere. Catalyst (50 to 400 ppm) and silane monomers (**MDMHSi**, **BDMAmMSi, L_2H**), silane polymer (**L_nH**), poly[hydrogenomethylsiloxane-*co*-dimethylsiloxane] (**P(DM-*co*-MH)**: **$MD_9D'_3M$**, **$MD_{85}D'_{0.25}M$** or poly(hydrogenomethyl)silane **$MD'_{105}M$** were mixed together in a Schlenk tube. The mixture was heated prior to the dropwise addition of the allylic compound (allyl functions / hydrogenosilane functions ratio =1 to 7). Poly[hydrogenomethylsiloxane-*co*-dimethylsiloxane] (**P(DM-*co*-MH)**) was selected for its short backbone and its random well defined structure **$MD_9D'_3M$** to make analysis easier. Time and temperature were varied as described in the results and discussion part.

Hydrosilylations of ***t*BAP** by **DCMSi** were performed in sealed tubes.

Hydrosilylation yield was measured by integration of the isolated signal of the methylene group in γ position of Si atom from ^{1}H NMR spectrum.

Poly[(3-(*tert*-butylperoxy)propyl)methylsiloxane-*co*-dimethylsiloxane] (^{1}H NMR 250MHz, $CDCl_3$) δ (ppm): 0.10 (Si-$C\underline{H}_3$), 0.50 (Si-$C\underline{H}_2$), 1.30 ($C(C\underline{H}_3)_3$), 1.60 (Si-CH_2-$C\underline{H}_2$), 3.90 ($C\underline{H}_2$-O) - (^{13}C NMR 250MHz, $CDCl_3$) δ (ppm): 1.2 ($Si(\underline{C}H_3)_2$), 2.0 ($Si(\underline{C}H_3)_3$), 13.8 (Si-$\underline{C}H_2$), 21.8 (Si-CH_2-$\underline{C}H_2$), 26.5 ($C(\underline{C}H_3)_3$), 77.6 ($\underline{C}H_2$-O), 80.1 ($\underline{C}(CH_3)_3$) – (^{29}Si NMR 250MHz, $CDCl_3$) δ (ppm): -22 ($\underline{Si}$-CH_2), -21 to -18 ($\underline{Si}$-CH_3), 7.5 ($\underline{Si}(CH_3)_3$).

Poly[(3-*tert*-butoxypropyl)methylsiloxane-*co*-dimethylsiloxane] (^{1}H NMR 250MHz, $CDCl_3$) δ (ppm): 0.10 (Si-$C\underline{H}_3$), 0.50 (Si-$C\underline{H}_2$), 1.20 ($C(C\underline{H}_3)_3$), 1.55 (Si-CH_2-$C\underline{H}_2$), 3.30 ($C\underline{H}_2$-O) - (^{13}C NMR 250MHz,

$CDCl_3$) δ (ppm): 1.2 (Si($\underline{C}H_3)_2$), 2.0 (Si($\underline{C}H_3)_3$), 13.8 (Si-$\underline{C}H_2$), 24.5 (Si-CH_2-$\underline{C}H_2$), 27.8 (C($\underline{C}H_3)_3$), 64.6 ($\underline{C}H_2$-O), 72.5 ($\underline{C}(CH_3)_3$).

6 – General procedure for thiol-ene reaction between ***t*BAP** and mercaptopropylsilane monomer

In a round bottom flask under argon were added **DM3PSi** (1.80 g, 10 mmol, 1eq.), ***t*BAP** (2.60 g, 20 mmol, 2 eq.) and bis(4-*tert*-butylcyclohexyl)peroxydicarbonate (0.8 g that is to say 1 mol.% in respect to **DM3PSi**). The mixture was heated at 43°C for 10 h. At the end of the reaction, the excess of ***t*BAP** was removed under vacuum (0.2 mmHg at room temperature).

(3-(3-(*Tert*-butylperoxy)propylthio)propyl)dimethoxy(methyl)silane (**BP3DM2Si**) (Figure 3):

(^{1}H NMR 250MHz, $CDCl_3$) δ (ppm): 0.10 (s, C$\underline{H}_3$-Si-C, 3H), 0.70 (m, C$\underline{H}_2$-Si, 2H), 1.20 (s, (C$\underline{H}_3)_3$-C, 9 H), 1.65 (m, Si-CH_2-C$\underline{H}_2$, 2H), 1.85 (m, C$\underline{H}_2$-CH_2-O, 1.5H), 2.50 (m, C$\underline{H}_2$-S-C$\underline{H}_2$, 3.8H), 3.50 (s, Si-O-C$\underline{H}_3$, 6H), 4.0 (t, C$\underline{H}_2$-O, 1.8H).

(^{29}Si NMR 250MHz, $CDCl_3$) δ (ppm): -1.7.

(^{13}C NMR 250MHz, CDCl3) δ (ppm): -5.6 (Si-$\underline{C}H_3$), 12.7 (Si-$\underline{C}H_2$), 23.2 ($\underline{C}H_2$-CH_2-CH_2-OO), 26.4 (($\underline{C}H_3)_3$-C), 28.3 (S-$\underline{C}H_2$-CH_2-CH_2-Si), 28.6 ($\underline{C}H_2$-CH_2-Si), 35.6 ($\underline{C}H_2$-CH_2-OO), 49.9 (Si-O$\underline{C}H_3$) 73.3 ($\underline{C}H_2$-OO), 80.2 (($CH_3)_3$-$\underline{C}$), 80.0 ($\underline{C}$-$(CH_3)_3$).

(3-(3-(*Tert*-butylperoxy)propylthio)propyl)trimethoxysilane (**BP3TDMSi**)

When **TM2PSi** was used instead of **DM3PSi**, all signals of **BP3DTM2Si** were similar except that no signal appeared at 0.10 ppm, and integration for Si-O-CH_3 signal was found to be equal to 9.

7 – Condensation of peroxide grafted silane monomer with hydroxyl *terminated* polysiloxane

BP3DM2Si (1 mmol, 1 eq.), **DMS-S15** (1 mmol, 1 eq.) and tin(II) ethylhexanoate (2 wt.% in respect to silane monomer) were mixed in a round bottom flask. The mixture was stirred for 24 h at room temperature under argon. The reaction with **BP3DM2Si** was performed under the same equimolar conditions. Polymers were precipitated from cold methanol, filtered and dried at 25°C (2.10^{-2} mmHg).

8 – Condensation of peroxide grafted silane monomer and hydride *terminated* polysiloxane

BP3DM2Si (1 mmol, 1 eq.), **DMS-H03** (1 mmol, 1 eq.) and $B(C_6F_5)_3$ (0.01 mmol, 0.01 eq.) were mixed in a round bottom flask. The mixture was stirred up to 48 h at room temperature or at 50°C.

9 – General procedure for thiol-ene reaction between ***t*BAP** and poly[dimethylsiloxane-*co*-mercaptopropylsiloxane] **SMS-042**

The procedure was similar for silane monomers and poly[dimethylsiloxane-*co*-mercaptopropylsiloxane] (**SMS-042**) except that solvent (toluene – 5 ml) was used. At the end of the reaction, the polymer was reprecipited from cold methanol, filtered and dried at 25°C (2.10^{-2} mmHg).

RESULTS AND DISCUSSION

Peroxide grafted PDMS were synthesized using the well-known reaction of hydrosilylation and the thiol-ene chemistry.

PEROXIDE GRAFTED PDMS *VIA* HYDROSILYLATION CHEMISTRY

Hydrosilylation of ***t*BAP** with **P(DM-*co*-MH)**s (See Supplemental Data Section) takes place as shown in Figure 1. The grafting yield was followed thanks to the α-CH_2 increasing signal of the grafted polysiloxane with ^{1}H NMR analysis. Surprisingly, according to usual experimental conditions (Speier's catalyst, 200 ppm, 70°C), integration of the α-CH_2 signal gave a grafting yield about 25% whatever the excess (2 to 7 eq.) of ***t*BAP** was. Nevertheless, a total consumption of Si-H groups indicated that a side reaction occurred during hydrosilylation.

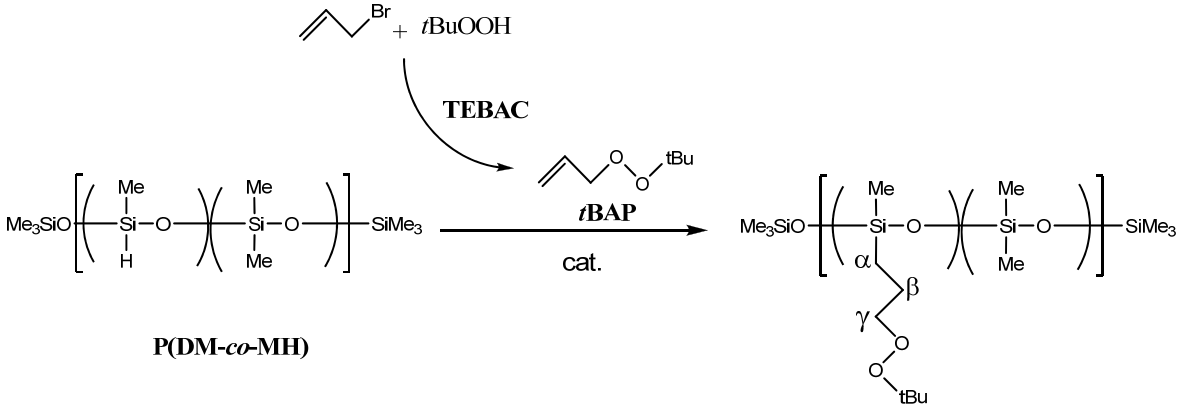


Figure 1. Hydrosilylation of **P(DM-*co*-MH)** by ***t*BAP**.

Identification of the side reaction

In order to identify side reaction, a model hydrosilylation reaction between ***t*BAP** and **$MD_9D'_3M$** (a well-defined poly[dimethylsiloxane-*co*-hydrogenomethylsiloxane] was deeply studied (Speier's catalyst, 200 ppm, 70°C, 5 eq. of ***t*BAP**). After 30 h, hydrogenosilane signals totally disappeared from ^{1}H NMR, ^{29}Si NMR and FT-IR spectrum. From ^{1}H and ^{29}Si NMR, hydrosilylation yield was found to be 26%. From ^{29}Si NMR spectra (See Supplemental Data Section), it was deduced that 22% of T units: Me-Si-(O-SiR_2-)$_3$ and 47% of Si-OR group were formed. T units were expected since viscosity of the media slightly increased and could be attributed to an imperfect anhydrous medium. The Si-OR groups were assigned to Si-O-C$(CH_3)_3$ moieties using ^{13}C NMR. Actually, in addition to expected signals due to hydrosilylation product (see in Supplemental Data Section), Si-O$\underline{C}(CH_3)_3$ signal was located at 72.8 ppm in ^{13}C NMR spectra and did not appear in the ^{13}C NMR DEPT analysis (See Supplemental Data Section) and Si-OC($\underline{C}H_3)_3$ signal was located at 31.9 ppm. These signals were attributed to reaction product of the O-silylation of *tert*-butanol, a by-product arising from the ***t*BAP** decomposition (Figure 2). Hydrosilylation and O-silylation could have been though to not simultaneously take place. Another explanation of the low observed yield could be attributed to the well known property of hydrosilane in reducing of peroxide groups. ^{29}Si NMR analysis was performed on a sample after only 3 h of reaction – that is to say with 23% of remaining unreacted hydrogenosilane functions. It appeared that 20% of hydrosilylated ***t*BAP** were formed but also 40% of Si-O*t*Bu and 17% of T units. It can be concluded that there is no kinetically preferred reaction.

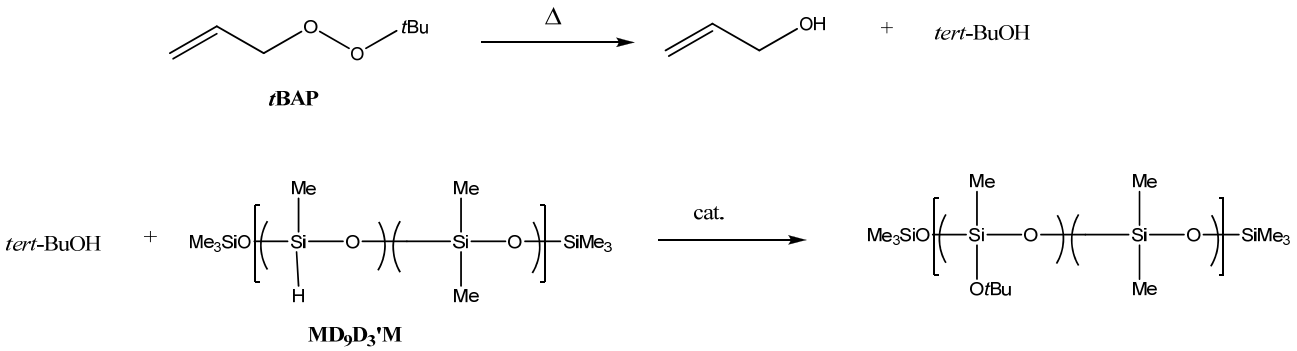


Figure 2. Main side reaction occuring during hydrosilylation: O-silylation of *tert*-butanol.

Since the side reaction of *tert*-butanol grafting occurs during hydrosilylation of **MD$_9$D'$_3$M** by ***t*BAP**, the reactivity of the peroxidic entity was hard to anticipate and it was then not possible to determine if an optimisation of the reaction parameters (catalyst – nature and quantity, temperature, polysiloxane architecture and so forth) could be reach. To overcome this, the hydrosilylation reaction was run with an allylic compound having a similar structure to that of ***t*BAP**: *tert*-butyl allylether (***t*BAE**). In a first step, hydrosilylation by ***t*BAE** confirmed the experimental procedure thanks to an usual reaction (Speier's catalyst, 200ppm, 70°C) that led to a 98% grafted copolymer in a couple of hours. Moreover, ***t*BAE** was engaged in a competitive reaction with ***t*BAP** in order to compare their reactivity. Initial ratio was 10% of ***t*BAP** and 90% of ***t*BAE** (unsaturation/hydrogenosilane function ratio = 5/1). After five hours, no more hydrogenosilane functions remained. Both hydrosilylation reactions occurred and the copolymer was grafted with (*tert*-butoxy)propyl group for 67% and with (*tert*-butylperoxy)propyl group for 17% (Table 1). Hydrogenomethylsiloxane functions that did not undergo hydrosilylation became T units and Si-O*t*Bu groups. Since grafting of peroxide group yield was close to the one observed in hydrosilylation by lonely ***t*BAP**, it was deduced that the reactivity of the ***t*BAP** was not a restrictive factor. Moreover, since initial composition ***t*BAE** / ***t*BAP** was 90/10 and final grafting yield was 67/17 (grafted ***t*BAE** / grafted ***t*BAP**), it can be deduced that ***t*BAP** is more reactive than ***t*BAE**. Otherwise, the minimum of ***t*BAE** grafting yield would have been 90%, keeping in mind that allylic species / Si-H functions ratio

was equal to 5. From that point of view, it could be possible to reach higher grafting yield of ***t*BAP** by an optimisation of the reaction parameters.

Table 1. Comparison of the ***t*BAP** and ***t*BAE** reactivities during hydrosilylation of **$MD_9D'_3M$** (5 mmol of allylic compound to 1 mmol of SiH).

Allylic compound	Grafting rate of SiH
***t*BAP** (100%)	26 %
***t*BAE** (100%)	98 %
***t*BAE**: 90% + ***t*BAP**: 10%	***t*BAE**: 67 % + ***t*BAP**: 17 %

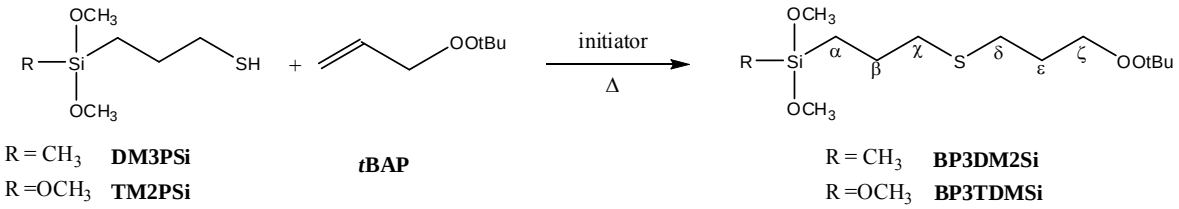
PEROXIDE GRAFTED PDMS *VIA* THIOL-ENE CHEMISTRY

Hydrosilylation enabled the synthesis of peroxide grafted polysiloxanes but yields remain disappointing in spite of the numerous attempts to enhance them. Hence, thiol-ene chemistry was studied as an alternative pathway either in the synthesis of reactive comonomer to polycondensation or in the reaction between PDMS and unsaturated compounds.

*Thiol-ene reaction between **tBAP** and silane monomers: a model reaction*

The first experiments with silane monomers (**DM3PSi**, **TM2PSi**), ***t*BAP** and bis(4-*tert*-butylcyclohexyl)peroxydicarbonate (Figure 3) were achieved to evaluate the feasibility of the reaction.

Since thiol-ene reaction is a radical pathway, a partial decomposition of ***t*BAP** could be induced on one hand by the decomposition of the added initiator and on the other hand by the heat required for the reaction (43°C, 10 h). As shown by the ^{1}H NMR spectra (Figure 4), none or less decomposition was observed since the shifts and integration of the signals were in good agreement with the predicted ones.



R = CH_3 **DM3PSi**
R =OCH_3 **TM2PSi**

***t*BAP**

R = CH_3 **BP3DM2Si**
R =OCH_3 **BP3TDMSi**

Figure 3. Thiol-ene reaction between mercaptopropyl silane monomer and ***t*BAP**.

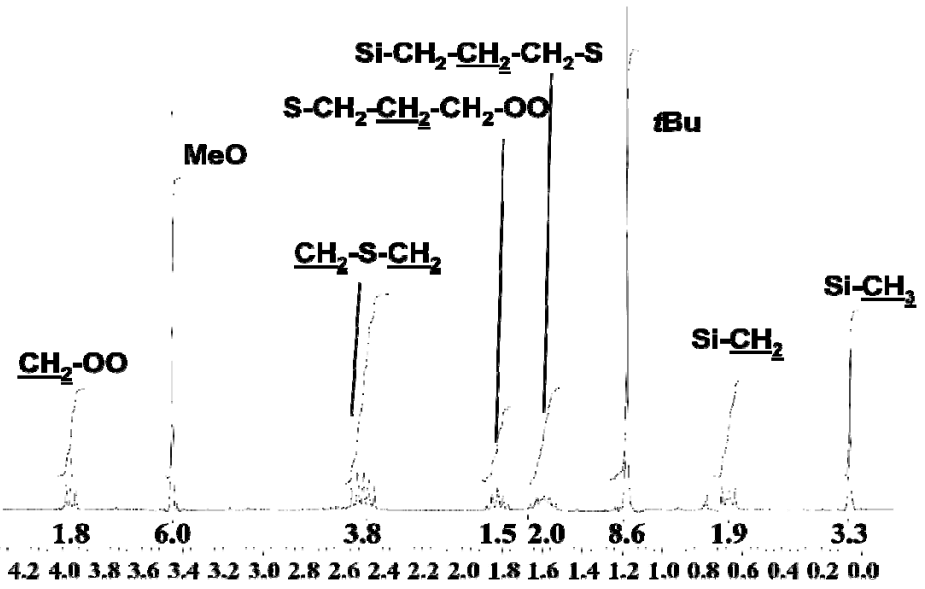


Figure 4. ^{1}H NMR of peroxide grafted silane monomer **BP3DM2Si**.

Not only none or less decomposition of the peroxide function was observed but thiol-ene reaction led to peroxide grafted silane monomer (**DM3PSi**) in good yields – 95% with bis(4-*tert*-butylcyclohexyl)peroxydicarbonate as initiator. Yields were calculated as the ratio $CH_{2\zeta}/CH_{2\alpha}$ (Figure 4) thanks to ^1H NMR, $CH_{2\alpha}$ (0.7 ppm) being representative of the starting material and $CH_{2\zeta}$ (4.0 ppm) being representative of the grafted moiety. Bis(4-*tert*-butylcyclohexyl)peroxydicarbonate was first chosen for its very low decomposition temperature ($T_{(t1/2=10h)}$ = 43°C). AIBN – which is interesting because it is a much more usual catalyst – was also used ($T_{(t1/2=10h)}$ = 59°C). It is to notice that in the latter case, the yields were about 85% (**DM3PSi**) but no decomposition of the peroxide group (grafted or not) was detected.

Since no decomposition was observed and no more thiol functions were detected at the end of the reaction, the ratio $CH_{2\zeta}/CH_{2\alpha}$ should have been 1, but both with bis(4-*tert*-butylcyclohexyl)peroxydicarbonate and AIBN, the ratios were found to be lower (0.95 and 0.85 respectively). This indicates that a side reaction occurred during the synthesis. As it is well known in thiol-ene chemistry, the recombination of the thiyl radical might occur during the reaction giving disulfide entities. This recombination should explained the non quantitative reaction since no more thiol groups were detected at the end of the reaction in FTIR spectroscopy (ν = 2570 cm^{-1}). A simple way to detect the disulfide group formed is RAMAN spectroscopy. The disulfide vibration wavelength was observed at 500 cm^{-1} as should be expected (Figure 5).

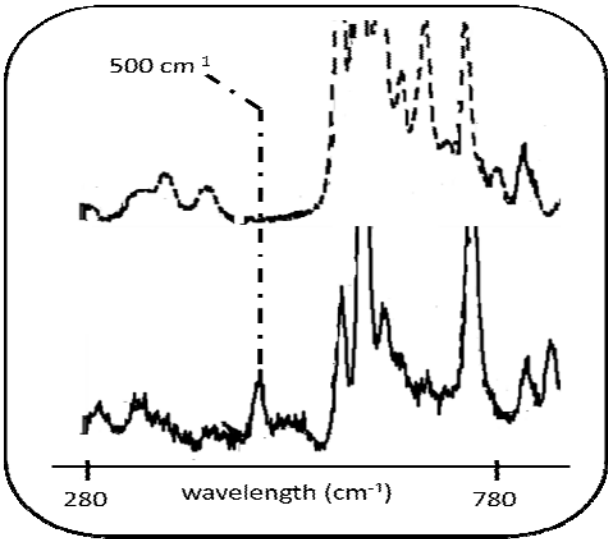


Figure 5. RAMAN spectroscopy of the starting mercaptosilane (broken line) and of the grafted silane (full line) – S-S zoom.

Polycondensation of peroxide grafted silane monomers: a pathway to peroxide grafted PDMS

The polymerization of silane monomers was carried out thanks to the alkoxy group *via* a condensation with α,ω-hydroxypolysiloxane **DMS-S15** (3 000 g.mol^{-1}). Stannous octanoate was chosen as condensation catalyst (Figure 6).

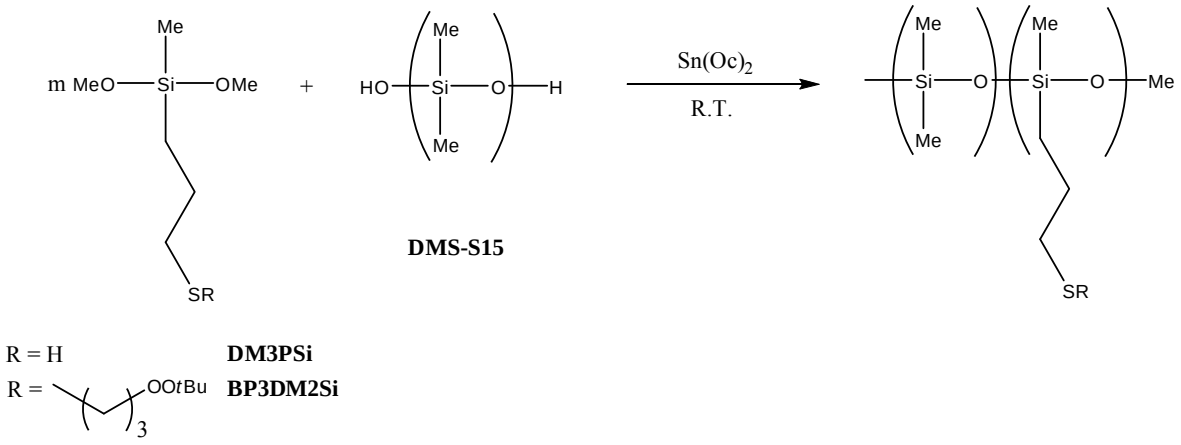


Figure 6. Polycondensation of peroxide grafted silane monomers with an α,ω-hydroxy-*terminated*-PDMS **DMS-S15**.

As it can be seen on SEC chromatogram (Figure 7), polycondensations were performed both with unmodified silane monomer **DM3PSi** and peroxide grafted silane monomer **BP3DM2Si** to inquire about the influence of the peroxide group. It is to notice that the condensation was better in the case of **DM3PSi** (27 500 $g.mol^{-1}$) whereas peroxide grafted monomer **BP3DM2Si** led to a 10 000 $g.mol^{-1}$ copolymer. It is difficult to consider a steric hindrance or an important difference in reactivity of the alkoxy groups between a silane monomer and peroxide grafted monomer. This difference of molar masses should be attributed to the influence of the peroxide functions on the catalyst activity. Considering SEC and ^{1}H NMR analysis, we could evaluate that an average of three peroxide groups per chain of polymer were inserted and that about 75% of the terminal groups were methoxy ones. These remaining alkoxy groups indicated that the polycondensation was chiefly limited by the reactivity of the alkoxy groups and could explain the low degree of polycondensation obtained even with **DM3PSi**. Actually, it was previously observed that the reactivity of the alkoxy groups varies with the number of alkoxy group linked to the silicon atom[9-11], as depicted in equation (5). The third alkoxy group can be considered as a "dead" functionality and trialkoxysilane are involved to yield linear polysiloxane[10].

$$RSi(OR')_3 > RR''Si(OR')_2 > RR''R'''Si(OR') \qquad (5)$$

$$\xrightarrow[\text{decreasing reactivity}]{}$$

Hence, during the polycondensation of the peroxide grafted dimethoxysilane **BP3DM2Si**, we supposed that once the first methoxy group reacted, the second one was no more sufficiently reactive to yield high molecular weight polymer. Considering the low reactivity of the second alkoxy group, it appeared to be interesting to achieve the condensation of peroxide grafted trialkoxysilane monomer: (3-(3-(*tert*-butylperoxy)propylthio)propyl)trimethoxysilane (**BP3DTM2Si)** with **DMS-S15**. Despite of its weak reactivity, the third alkoxy group was reactive towards silanol functions enough to lead to a crosslinked material. This strategy remained inefficient to give the grafted linear copolymer.

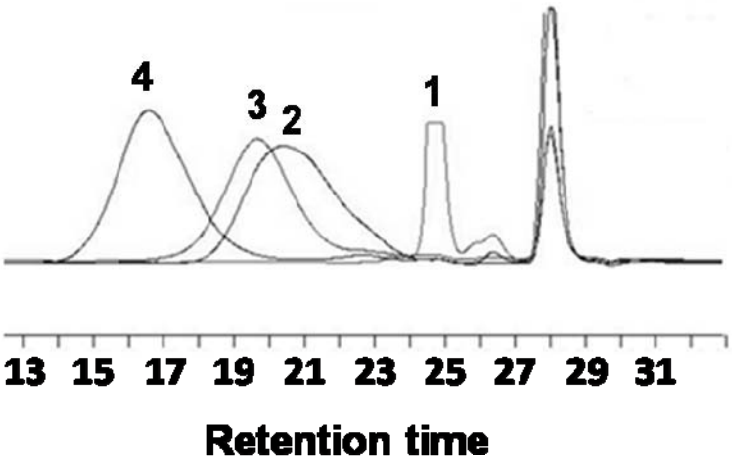


Figure 7. SEC analysis (1) peroxide grafted silane monomer **DM3PSi** (2) **DMS-S15** (3) condensation of peroxide grafted silane monomer **BP3DM2Si** with **DMS-S15** (4) condensation of silane monomer **DM3PSi** with **DMS-S15**.

An other kind of polycondensation between the peroxide grafted dialkoxysilane **BP3DM2Si** and an hydride-*terminated*-polydimethylsiloxane **DMS-H03** catalysed by $B(C_6F_5)_3$ was tried to reach a higher degree of polycondensation (Figure 8).

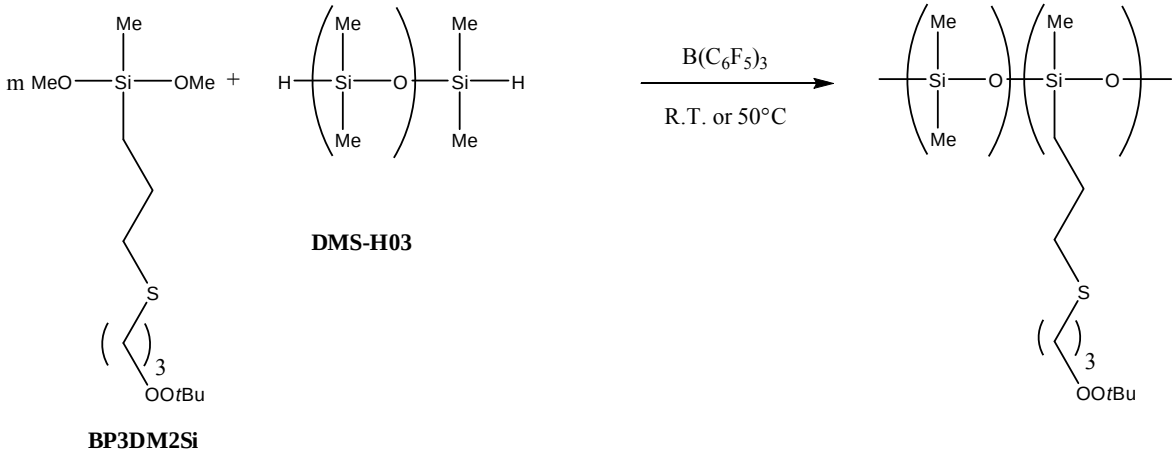


Figure 8. Polycondensation of peroxide grafted **BP3DM2Si** with **DMS-H03**.

This system was successfully employed in the condensation of alkoxysilane with organo-hydrosilane[12]. In our case, no condensation was observed even after 48 h at 50°C. We can suppose a poisoning of the catalyst by peroxide groups which might be able to complex the boron atom as was previously observed with $B(C_6F_5)_3$ as a hydrosilylation catalyst.

*Grafting of poly[dimethylsiloxane-*co*-mercaptopropylsiloxane] by thiol-ene reaction*

Thiol-ene reaction is another synthetic route to obtain peroxide grafted polysiloxane from commercial poly[dimethylsiloxane-*co*-mercaptopropylsiloxane] **SMS-042** and ***t*BAP** (Figure 9).

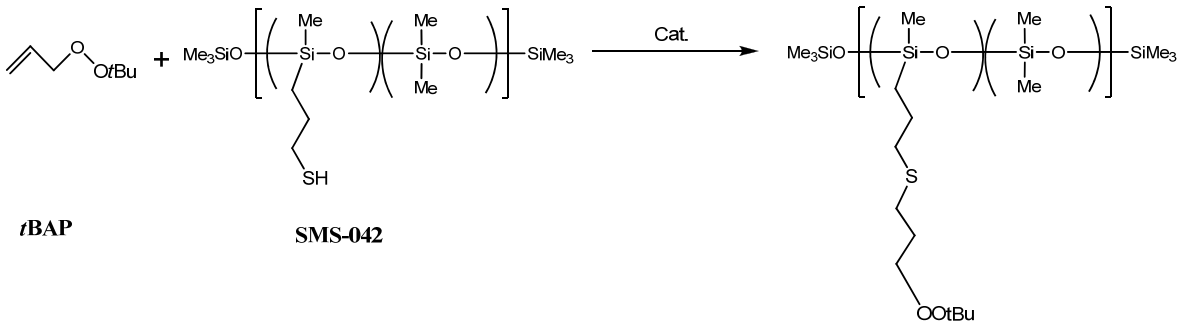


Figure 9. TBAP grafting onto **SMS-042** by thiol-ene reaction.

In rigorously same conditions for **SMS-042** than for silane monomers, the grafting yield was limited to about 30%. This was attributed to the previously identified disulfide group formation since viscosity of the reaction mixture increased. Further attempts (Table 2) were realized to raise the yield by varying the nature and quantity of catalyst, reaction time, temperature, media or atmosphere. Even with 5 eq. of ***t*BAP** (Table 2, entry 9) which should have promoted thiol-ene reaction, yield was not enhanced.

Whatever the conditions the grafting yield remained about 30% and the grafting was rather promoted than recombination of thyil radicals.

Table 2. Thiol-ene reaction between ***t*BAP** and **SMS-042**.

Exp	Initiator (mol. %)	***t*BAP** (eq.)*	T (°C)		t (h)	Solvent	Grafting (%)
1	Carbonate (1)	2	43	Argon	5	Toluene	34
2	Carbonate (1)	2	43	Argon	10	Toluene	35
3	Carbonate (1)	2	50	Argon	10	Toluene	30
4	Carbonate (1)	2	43	Argon	5	-	28
5	Carbonate (2)	2	43	Argon	5	Toluene	33
6	Carbonate (2)	2	43	Argon	10	Toluene	33
7	Carbonate (2)	2	43	Air	10	Toluene	0
8	AIBN (1)	2	59	Argon	10	-	30
9	Carbonate (1)	5	43	Argon	10	Toluene	33

*: equivalent per mole of thiol functions.

STUDY OF THE DECOMPOSITION OF THE GRAFTED PEROXIDE GROUP

The decomposition of peroxide group was studied with peroxide compound ***t*BAP** and peroxide grafted silane compound **BP3DM2Si**. The decomposition of **BP3DM2Si** was realized under argon atmosphere at 200°C for 5 min and led to the formation of (3-(3-

(hydroxy)propylthio)propyl)dimethoxy(methyl)silane (**HP2DM2Si**) (Figure 10) which have been identified with ^{1}H NMR thanks to the methylene group in α position of the hydroxyl group which is expected at about 3.7 ppm. Residual products and collected vapors were also analyzed by ^{1}H NMR spectroscopy. As expected, almost no more *tert*-butanol signal (1.2 ppm) appeared on residue spectrum and C<u>H$_2$</u>-OO*t*Bu signal (4.0 ppm) was shifted to 3.8 ppm corresponding to S-CH$_2$-CH$_2$-C<u>H$_2$</u>-OH issue from the abstraction of a proton by S-CH$_2$-CH$_2$-CH$_2$O•. From ^{1}H NMR analysis of the collected vapours the ratios of *tert*-butanol and acetone were 88.7 and 11.3% respectively.

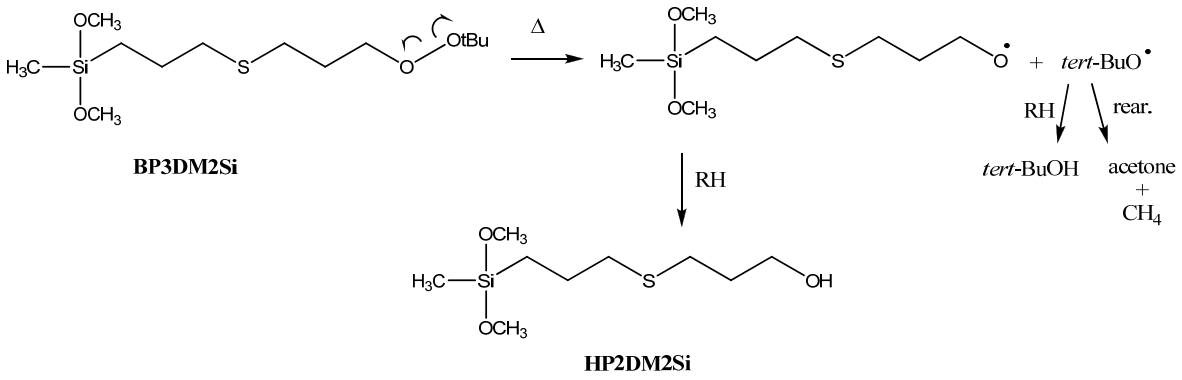


Figure 10. Decomposition of **BP3DM2Si**.

Study of the decomposition of the peroxide silane compounds by DSC analysis

DSC analysis led the characterization of the decomposition of peroxide silane and the calculation of the activation energy of the peroxide grafted silane monomer **BP3DM2Si**. We obtained $K_d=9.89.10^9e(-85/RT)$, hence E_a was found to be 85 kJ.mol^{-1}. This value of activation energy is slightly lower than those usually observed for peroxide compounds. The same DSC measurement was achieved in the case of the peroxide grafted silicone (25 % grafted **MD$_9$D'$_3$M** copolymer, 70°C, Speier's catalyst, 200ppm). It can be seen that the decomposition of the peroxidic groups begin at 105°C. Hence, we deduced the dissociation constant $k_d = 1.64.10^{10}e^{(-107/RT)}$ and the activation energy was found to be Ea = 107 kJ.mol^{-1}.

Conclusion

In the present paper peroxide grafted PDMS were synthesized by hydrosilylation of the *tert*-butyl allylperoxide. Characterizations were performed using ^{1}H NMR, ^{29}Si NMR, ^{13}C NMR and FT-IR. This enabled us to highlight a reduced reactivity due to different side reactions that were identified. Among them, O-silylation of entities derived from the decomposition of the peroxide was deduced from analysis and was delicate to control. Actually, on one hand heating is required to run the hydrosilylation but on the other hand promotes the peroxide decomposition. Further attempts to overcome this O-silylation were made by testing different catalysts. Hydrosilylations were performed using various catalytic systems: transition metal complexes catalysis, supported metal catalysis, Lewis acid-assisted catalysis or initiated by free radical. Moreover, influences of catalyst, temperature of the reaction, quantities of catalyst and silicone architecture were studied. We showed that it is possible to obtain a 25% peroxide grafted macroinitiator thanks to hydrosilylation.

We also developed a new synthesis of peroxide grafted silicone by a thiol-ene radical process and showed that thiyl radical recombination slightly occurs in these conditions. No induced decomposition of the ***t*BAP** was observed. Whereas the reaction between ***t*BAP** and silane monomers **BP3DM2Si** occured in good yields, and further polymerization led to peroxide grafted silicone polymers, grafting of the commercial poly[dimethylsiloxane-*co*-mercaptopropylsiloxane] **SMS-042** was limited up to 35%. Thermal decomposition of **BP3DM2Si** occurred with an usual peroxide decomposition mechanism but also revealed a low activation energy.

REFERENCES

1. Inoue, H.; Ueda, A.; Nagai, S. Journal of Polymer Science, Part A: Polymer Chemistry 1988, 26, (4), 1077-92.

2. Baysal, B. M.; Uyanik, N.; Hamurcu, E. E.; Cvetkovska, M. Journal of Applied Polymer Science 1996, 60, (9), 1369-1378.

3. Crivello, J. V.; Conlon, D. A.; Lee, J. L. Journal of Polymer Science, Part A: Polymer Chemistry 1986, 24, (6), 1197-215.

4. Crivello, J. V.; Lee, J. L.; Conlon, D. A. Journal of Polymer Science, Part A: Polymer Chemistry 1986, 24, (6), 1251-79.

5. Clouet, G.; Kayser, D. Journal of Polymer Science, Part A: Polymer Chemistry 1993, 31, (13), 3387-96.

6. Marciniec, B. In Comprehensive Hanbook on Hydrosilylation. Pergamon Press: Oxford, 1992.

7. Hoyle, C. E.; Lee, T. Y.; Roper, T. Journal of Polymer Science, Part A: Polymer Chemistry 2004, 42, 5301-5338.

8. Moulines, J.; Bougeois, M. J.; Campagnole, M.; Lamidey, A. M.; Maillard, B.; Montaudon, E. Synthetic Communications 1990, 20, (3), 349-53.

9. Sprung, M. M.; Guenther, F. O. Journal of the American Chemical Society 1955, 77, 3990-6.

10. Boutevin, B.; Youssef, B.; Abdellah, L.; Dinia, N. M. European Polymer Journal 1996, 32, (6), 701-708.

11. Abdellah, L. Synthèse et application de polymère photoréticulable. PhD Université Montpellier 2, 1991.

12. Rubinsztajn, S.; Cella, J. A. Polymer Preprints (American Chemical Society, Division of Polymer Chemistry) 2004, 45, (1), 635-636.

Table of Contents

Peroxide grafted PDMS: hydrosilylation reaction study and thiol-ene chemistry as an alternative pathway

PATRICE LUCAS, ETIENNE FLEURY, JEAN-FRANÇOIS ESTUR, VINCENT LAPINTE, JEAN-JACQUES ROBIN